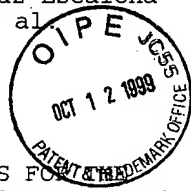


IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Antonio Muñoz-Escalona ) Group: 1755  
Lafuente, et al )  
Serial No.: 09/299,539 ) Examiner: not yet assigned  
Filed: April 26, 1999 ) Our Ref: B-3643 617072-2  
For: "CATALYTIC SYSTEMS FOR ) Date: October 7, 1999  
POLYMERIZATION AND COPOLYMERIZATION )  
OF ALPHA-OLEFINS" )



CLAIM TO PRIORITY UNDER 35 U.S.C. 119

Hon Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

[X] Applicant hereby makes a right of priority claim under 35  
U.S.C. 119 for the benefit of the filing date(s) of the  
following corresponding foreign application(s):

<u>COUNTRY</u>	<u>FILING DATE</u>	<u>SERIAL NUMBER</u>
EPO	April 27, 1998	98500101.5

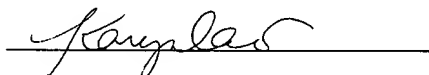
TC 1700 MAIL ROOM

OCT 15 1999


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- [ ] A certified copy of each of the above-noted patent  
applications was filed with the Parent Application  
No. \_\_\_\_\_.
- [X] To support applicant's claim, a certified copy of the above-  
identified foreign patent application is enclosed herewith.
- [ ] The priority document will be forwarded to the Patent Office  
when required or prior to issuance.

I hereby certify that this correspondence  
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Postal Service with sufficient postage as  
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Trademarks, Washington, D.C. 20231",  
on October 7, 1999 by Karyn Lao



Respectfully submitted,

  
John Palmer  
Attorney for Applicant  
Reg. No. 36,885

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Bescheinigung

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Attestation

Die angehefteten Unterla-  
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The attached documents  
are exact copies of the  
European patent application  
described on the following  
page, as originally filed.

Les documents fixés à  
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conformes à la version  
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européen spécifiée à la  
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Patentanmeldung Nr. Patent application No. Demande de brevet n°

98500101.5

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Der Präsident des Europäischen Patentamts:  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

*Alette Fiedler*

A. Fiedler

DEN HAAG, DEN  
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LA HAYE, LE

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**Blatt 2 der Bescheinigung**  
**Sheet 2 of the certificate**  
**Page 2 de l'attestation**

Anmeldung Nr.:  
Application no.:  
Demande n°: 98500101.5

Anmeldetag:  
Date of filing: 27/04/98  
Date de dépôt:

Anmelder:  
Applicant(s):  
Demandeur(s):  
REPSOL QUIMICA S.A.  
E-28046 Madrid  
SPAIN

Bezeichnung der Erfindung:  
Title of the invention:  
Titre de l'invention:

Catalytic systems for the polymerization and copolymerization of alpha-olefins

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:  
State:  
Pays:

Tag:  
Date:  
Date:

Aktenzeichen:  
File no.  
Numéro de dépôt:

Internationale Patentklassifikation:  
International Patent classification:  
Classification internationale des brevets:

C08F10/00, C08F4/602

Am Anmeldetag benannte Vertragsstaaten:  
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE  
Etats contractants désignés lors du dépôt:

Bemerkungen:  
Remarks:  
Remarques:

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## CATALYTIC SYSTEMS FOR THE POLYMERIZATION AND COPOLYMERIZATION OF ALPHA-OLEFINS

The present invention relates to a heterogeneous catalytic system and its use in olefin polymerization.

### 5 STATE OF THE ART

It is very well known that homogeneous catalytic systems present a disadvantage, when they are used in suspension polymerization processes, a part of the produced polymer adheres to the reactor walls; this effect is technically called "reactor fouling". Besides, in most cases, the particle size of the obtained polymer is very small and the bulk density is low, thus the industrial production is reduced. In order to prevent the reactor from fouling and to control the size and the morphology of the polymer particles which are formed, the homogeneous system can be supported on an inorganic oxide.

In the last years different preparatory strategies have been used in order to reach this aim. EPA-206794 (Exxon) discloses a catalyst which comprises a carrier, a metallocene, and an alumoxane. The carrier is first treated with alumoxane and then the metallocene is added. EP-A-295312 (Mitsui) discloses a catalyst consisting of a carrier wherein alumoxane is precipitated and then the resulting material is impregnated with a metallocene. No additional cocatalyst is used in the polymerization process.

The first application claiming a process wherein the metallocene is reacted with the support surface is EP 293815 (HOECHST). The metallocene contains a SiOR group that reacts with the OH groups on the surface of the support.

EP 757053 (HOECHST) supports the metallocene by reacting the hydroxyls of the inorganic support with a metallocene which contains a M-R-Z-Cl group, wherein M is Si, Ge or Sn and Z is B, Si, Ge or Sn. EP 757992 (REPSOL) discloses a catalyst comprising a metallocene which contains a Si-Cl group to react with the hydroxyls of the inorganic support.

Object of the present invention is the preparation of a supported catalyst for (co)polymerization of ethylene, whose activity is not decreased by the heterogeneization process and which results in a polymer having a very good morphology.

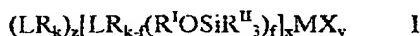
Thanks to the methods described in the present invention, heterogeneous catalysts can be obtained; they allow to effectively control the morphology and the distribution of particle sizes, with a regular growth of the polymer around the catalyst particles and without reactor fouling.

### 30 DETAILED DESCRIPTION OF THE INVENTION.

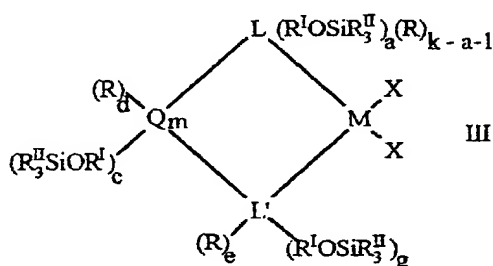
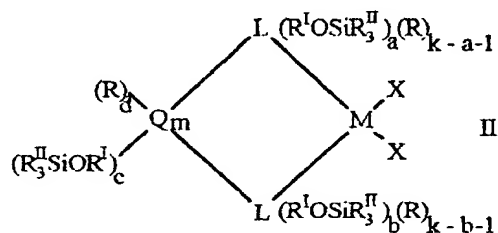
The present invention relates to heterogeneous catalytic systems obtained by reacting a specific class of metallocene compounds with a treated porous inorganic support, i.e. a support having on its surface an alumoxane.

2

According to the present invention the specific class of metallocene compounds is defined by general formulas I, II and III.



5



wherein:

- 10 L, equal to or different from each other, is selected from the group comprising: cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl and benzoindenyl;
- each R is independently selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl, linear or branched, optionally substituted by 1 to 10 halogen atoms, or a group SiR<sup>II</sup><sub>3</sub>;
- 15 each R<sup>I</sup>, equal to or different from each other, is a divalent aliphatic or aromatic hydrocarbon group containing from 1 to 20 carbon atoms, optionally containing from 1 to 5 heteroatoms of groups 14 to 16 of the periodic table of the elements and boron; preferably it is: C<sub>1</sub>-C<sub>20</sub> alkylene, C<sub>3</sub>-C<sub>20</sub> cycloalkylene, C<sub>6</sub>-C<sub>20</sub> arylene, C<sub>7</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkylene, or alkylarylene, linear or branched, or a group SiR<sup>II</sup><sub>2</sub>;
- each R<sup>II</sup> is independently selected from C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl or C<sub>7</sub>-C<sub>20</sub> alkylaryl, linear or branched; preferably R<sup>II</sup> is methyl, ethyl, isopropyl;
- 20 each Q is independently selected from B, C, Si, Ge, Sn;
- M is a metal of group 3, 4 or 10 of the Periodic Table, Lanthanide or Actinide; preferably it is titanium, zirconium or hafnium;



## 3

each X is independently selected from: hydrogen, chlorine, bromine,  $\text{OR}^{\text{II}}$ ,  $\text{NR}^{\text{II}}_2$ ,  $\text{C}_1\text{-C}_{20}$  alkyl or  $\text{C}_6\text{-C}_{20}$  aryl;

$\text{L}'$  is N or O;

k depends of the type of L; more specifically when L is cyclopentadienyl k is equal to 5, when L is indenyl k is equal to 7, when L is fluorenyl or benzoindenyl k is equal to 9, when L is tetrahydroindenyl k is equal to 11 and when L is octahydrofluorenyl, k is equal to 17;

z is equal to 0, 1 or 2;

x is equal to 1, 2 or 3;

y is equal to 1, 2 or 3;

10  $x + y + z$  is equal to the valence of M,

m is an integer which can assume the values 1, 2, 3 or 4;

a and b are integers whose value ranges from 0 to k-1;

f is an integer whose value ranges from 1 to k;

g is an integer whose value ranges from 0 to 1;

15 c and e are equal to 0 or 1;

$a + b + c$  is at least 1;

$a + g + c$  is at least 1;

d is equal to 0, 1 or 2;

when Q is B, then  $c + d = 1$ ;

20 when Q is C, Si, Ge or Sn, then  $c + d = 2$ ;

when  $\text{L}'$  is N, then  $g + e = 1$ ;

when  $\text{L}'$  is O, then  $g = 0$  and  $e = 0$ .

Non limitative examples of  $\text{R}^{\text{I}}\text{OSiR}^{\text{II}}_3$  are:

$\text{CH}_2\text{-CH}_2\text{-OSiMe}_3$ ;  $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ;  $\text{CH}_2\text{-O-CH}_2\text{-OSiMe}_3$ ;  $\text{O-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ;  $\text{SiMe}_2\text{-}$

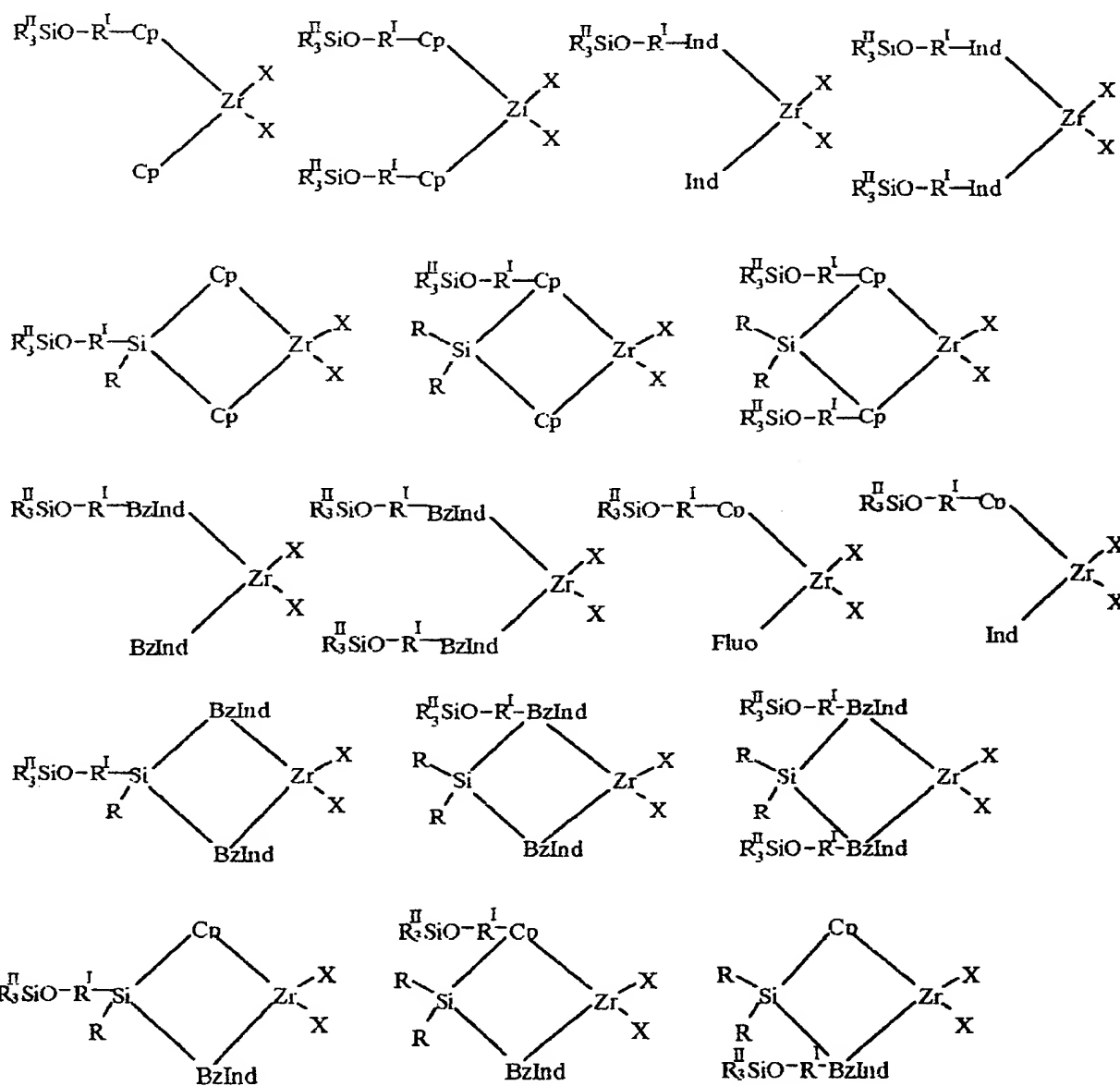
25  $\text{CH}_2\text{-CH}_2\text{-OSiMe}_3$ ;  $\text{CH}_2\text{-C}_6\text{H}_5\text{-CH}_2\text{-OSiMe}_3$ ;  $\text{CH(C}_6\text{H}_5\text{)-CH}_2\text{-OSi(C}_6\text{H}_5\text{)}_2\text{Me}$ ;  $\text{C(CH}_3\text{)}_2\text{-C(CH}_3\text{)}_2\text{-OSi(PhMe)}_3$ ;  $\text{CH(CH}_3\text{)-CH(CH}_3\text{)-O-SiEtMe}_2$ ;  $\text{SiMe}_2\text{-OSiMe}_3$ .

Preferably the group  $\text{R}^{\text{I}}\text{OSiR}^{\text{II}}_3$  is selected from  $\text{CH}_2\text{-CH}_2\text{-OSiMe}_3$ ,  $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ,  $\text{CH}_2\text{-O-CH}_2\text{-OSiMe}_3$ ,  $\text{O-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ,  $\text{SiMe}_2\text{-CH}_2\text{-CH}_2\text{-OSiMe}_3$ ,  $\text{SiMe}_2\text{-OSiMe}_3$ .

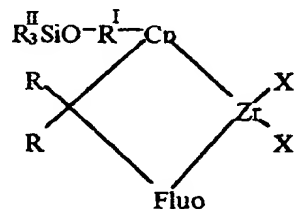
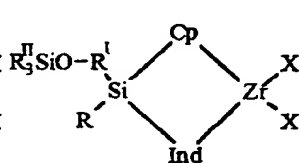
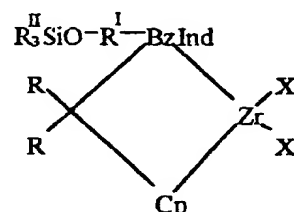
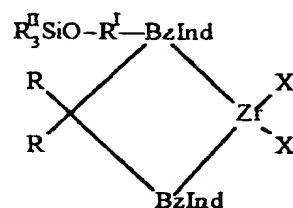
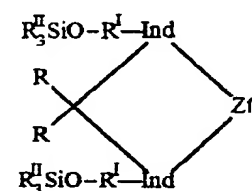
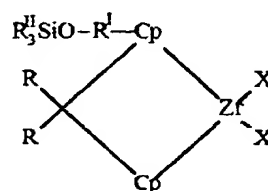
Preferred structures of compounds of formula I, II and III are the following:

30

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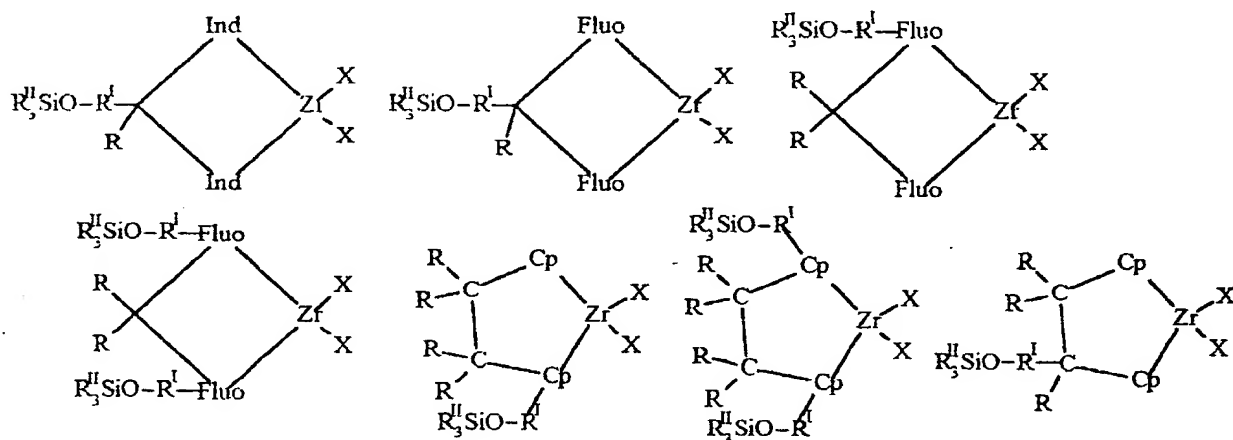


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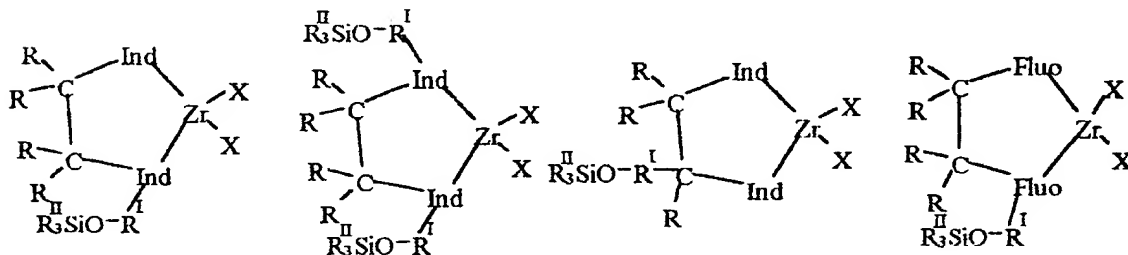


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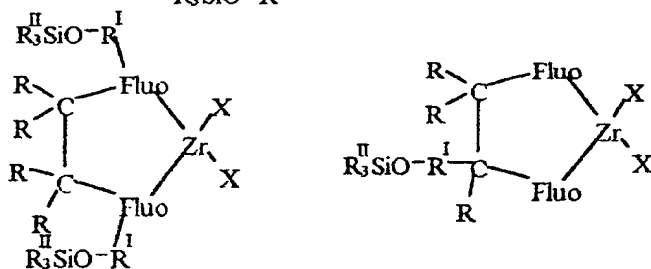
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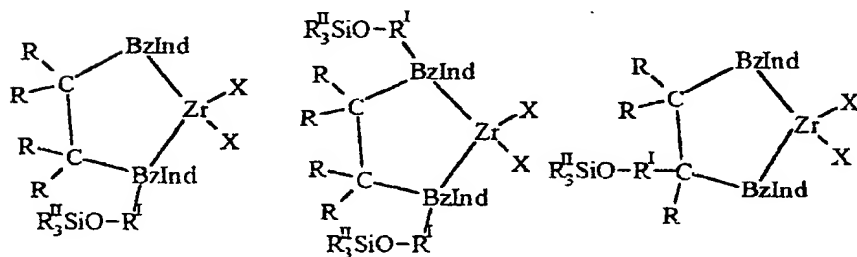
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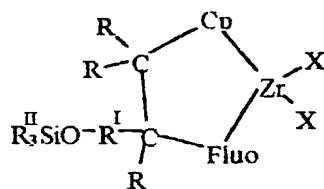
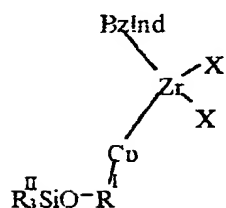
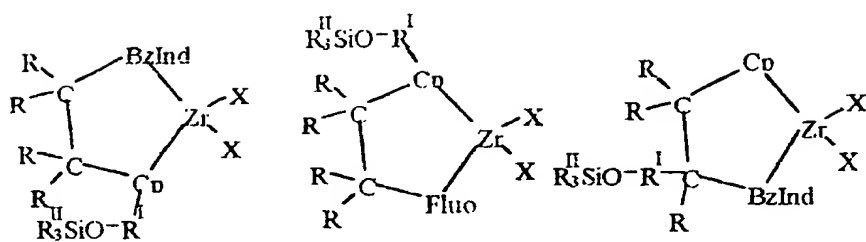
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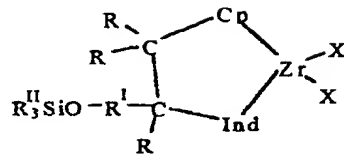
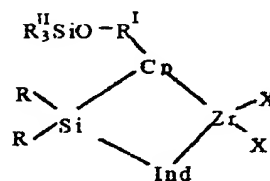
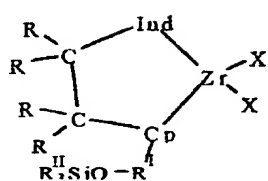
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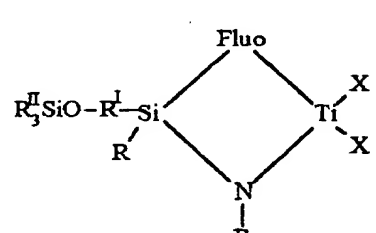
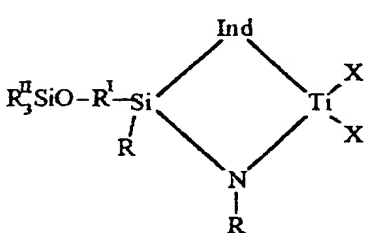
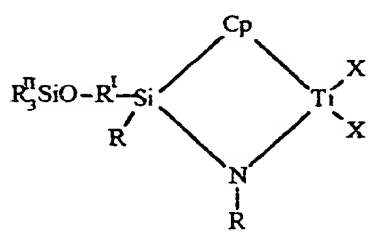
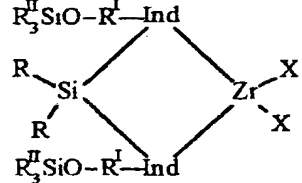
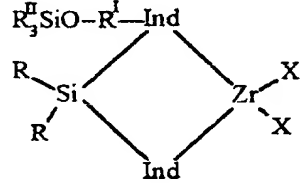
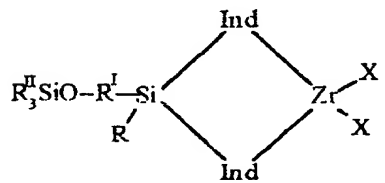
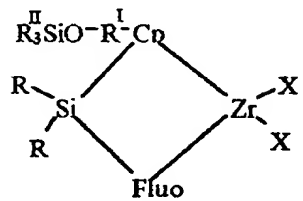
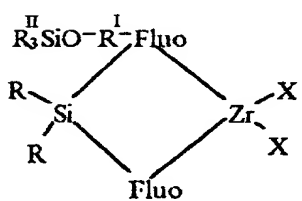
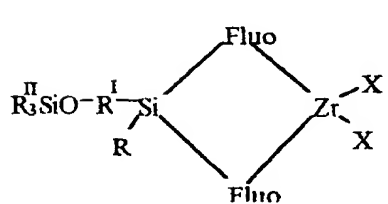
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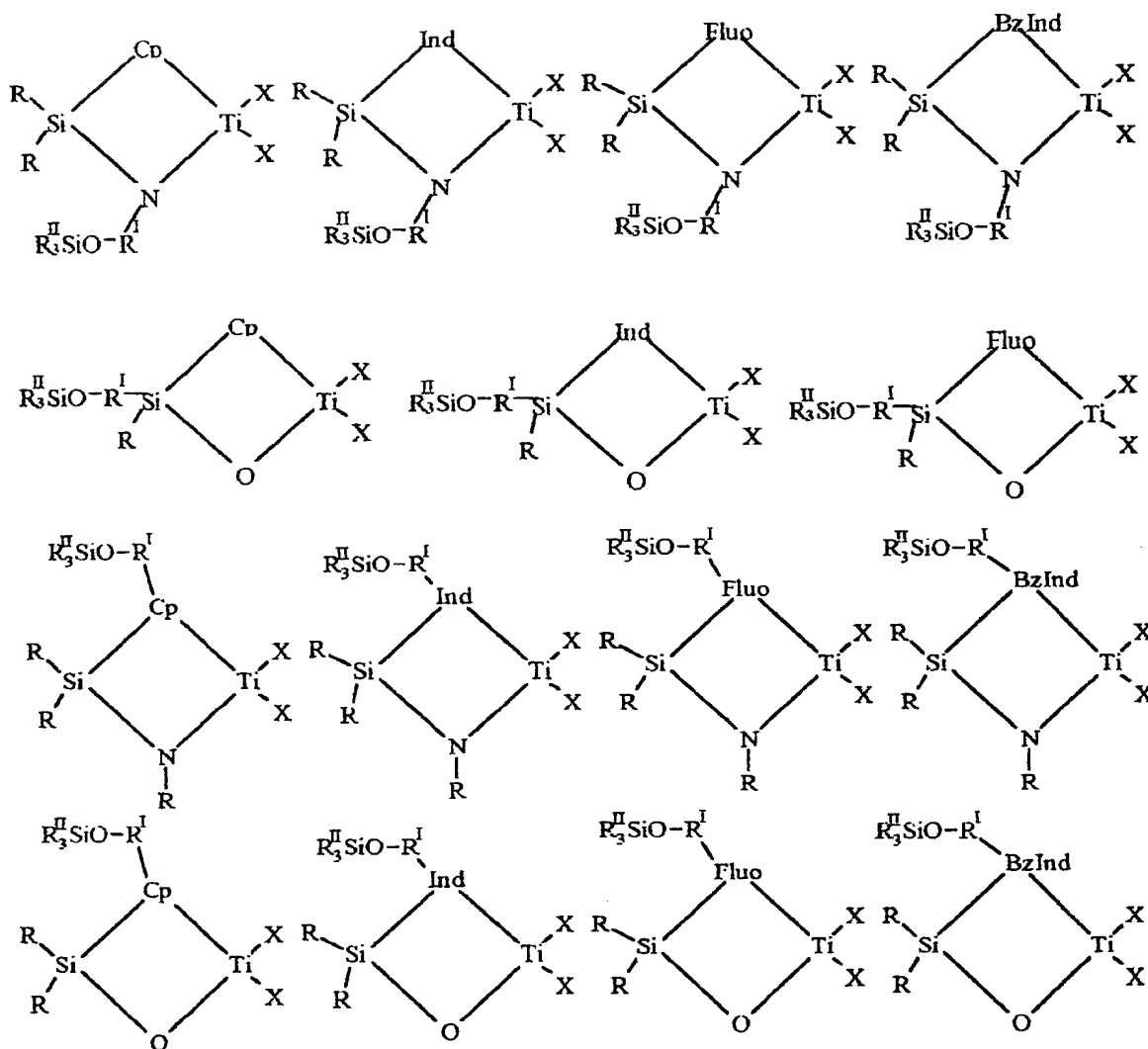


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- 5 Wherein Cp, Ind, BzInd and Fluo indicate respectively a cyclopentadienyl, indenyl, benzoindenyl and fluorenyl ring optionally substituted by C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl or C<sub>7</sub>-C<sub>20</sub> alkylaryl; the maximum number of substituents depends on the amount of hydrogen which can be substituted; R, R<sup>I</sup>, R<sup>II</sup> and X have the above indicated meaning.

Preferred compounds for use in the present invention are the following:

- 10 bis(trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;  
 (trimethylsiloxyethyl-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride;  
 (trimethylsiloxyethyl-cyclopentadienyl)(indenyl) zirconium dichloride;  
 (trimethylsiloxyethyl-cyclopentadienyl)(2-methyl-indenyl) zirconium dichloride;  
 (trimethylsiloxyethyl-cyclopentadienyl)(fluorenyl) zirconium dichloride;

(trimethylsiloxyethyl-cyclopentadienyl)(9-methyl-fluorenyl) zirconium dichloride;  
(trimethylsiloxyethyl-cyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride;

bis(trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;

5 (trimethylsiloxypropyl-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride ;

(trimethylsiloxypropyl-cyclopentadienyl)(indenyl) zirconium dichloride,

(trimethylsiloxypropyl-cyclopentadienyl)(2-methyl-indenyl) zirconium dichloride;

(trimethylsiloxypropyl-cyclopentadienyl)(fluorenyl) zirconium dichloride;

(trimethylsiloxypropyl-cyclopentadienyl)(9-methyl-fluorenyl) zirconium dichloride;

10 (trimethylsiloxypropyl-cyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride;

bis(trimethylsiloxy-methoxy-cyclopentadienyl) zirconium dichloride;

(trimethylsiloxy-methoxy-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride ;

(trimethylsiloxy-methoxy-cyclopentadienyl)(indenyl) zirconium dichloride;

15 (trimethylsiloxy-methoxy-cyclopentadienyl)(2-methyl-indenyl) zirconium dichloride;

(trimethylsiloxy-methoxy-cyclopentadienyl)(fluorenyl) zirconium dichloride;

(trimethylsiloxy-methoxy-cyclopentadienyl)(9-methyl-fluorenyl) zirconium dichloride;

(trimethylsiloxy-methoxy-cyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride;

20 bis(trimethylsiloxy-ethoxy-cyclopentadienyl) zirconium dichloride;

(trimethylsiloxy-ethoxy-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride ;

(trimethylsiloxy-ethoxy-cyclopentadienyl)(1-indenyl) zirconium dichloride;

(trimethylsiloxy-ethoxy-cyclopentadienyl)(2-methyl-indenyl) zirconium dichloride;

(trimethylsiloxy-ethoxy-cyclopentadienyl)(fluorenyl) zirconium dichloride;

25 (trimethylsiloxy-ethoxy-cyclopentadienyl)(9-methyl-fluorenyl) zirconium dichloride;

(trimethylsiloxy-ethoxy-cyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride;

bis(trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl) zirconium dichloride;

(trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride;

30 (trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(indenyl) zirconium dichloride,

(trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(2-methyl-indenyl) zirconium dichloride;

(trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(fluorenyl) zirconium dichloride;

(trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(9-methyl-fluorenyl) zirconium dichloride;

(trimethylsiloxy-ethyl-(dimethyl)silyl-cyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride;

35 bis(trimethylsiloxy-(dimethyl)silyl-cyclopentadienyl) zirconium dichloride;

(trimethylsiloxy-(dimethyl)silyl-cyclopentadienyl)(cyclopentadienyl) zirconium dichloride;

dimethylsilandiybis(2-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;

dimethylsilandiybis(3-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;

5 dimethylsilandiy(3-trimethylsiloxyethyl-cyclopentadienyl) (cyclopentadienyl) zirconium dichloride;

dimethylsilandiy(2-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;

dimethylsilandiy(3-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;

dimethylsilandiy(1-(3-trimethylsiloxyethyl-indenyl))(cyclopentadienyl) zirconium dichloride;

dimethylsilandiy(2-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

10 dimethylsilandiy(3-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilandiy(2-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

dimethylsilandiy(3-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

dimethylsilandiy(2-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

dimethylsilandiy(3-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

15 dimethylsilandiy(3-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium dichloride;

dimethylsilandiybis(2-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;

dimethylsilandiybis(3-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;

dimethylsilandiy(3-trimethylsiloxypropyl-cyclopentadienyl) (cyclopentadienyl) zirconium dichloride;

20 dimethylsilandiy(1-(3-trimethylsiloxypropyl-indenyl)) (cyclopentadienyl) zirconium dichloride;

dimethylsilandiy(2-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;

dimethylsilandiy(3-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;

dimethylsilandiy(2-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilandiy(3-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;

25 dimethylsilandiy(2-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

dimethylsilandiy(3-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

dimethylsilandiy(2-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

dimethylsilandiy(3-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

dimethylsilandiy(3-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium

30 dichloride,

dimethylsilandiybis(2-trimethylsiloxy-methoxy-cyclopentadienyl) zirconium dichloride;

dimethylsilandiybis(3-trimethylsiloxy-methoxy-cyclopentadienyl) zirconium dichloride;

dimethylsilandiy(2-trimethylsiloxy-methoxy-cyclopentadienyl)(1-indenyl) zirconium dichloride;

35 dimethylsilandiy(3-trimethylsiloxy-methoxy-cyclopentadienyl)(1-indenyl) zirconium dichloride;



- dimethylsilandiyl(2-trimethylsiloxy-methoxy-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
 dimethylsilandiyl(3-trimethylsiloxy-methoxy-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
 dimethylsilandiyl(2-trimethylsiloxy-methoxy-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 dimethylsilandiyl(3-trimethylsiloxy-methoxy-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
- 5 dimethylsilandiyl(2-trimethylsiloxy-methoxy-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
 dimethylsilandiyl(3-trimethylsiloxy-methoxy-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 10 dimethylsilandiylbis(2-trimethylsiloxy-ethoxy-cyclopentadienyl) zirconium dichloride;  
 dimethylsilandiylbis(3-trimethylsiloxy-ethoxy-cyclopentadienyl) zirconium dichloride;  
 dimethylsilandiyl(2-trimethylsiloxy-ethoxy-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 dimethylsilandiyl(3-trimethylsiloxy-ethoxy-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 dimethylsilandiyl(2-trimethylsiloxy-ethoxy-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;
- 15 dimethylsilandiyl(3-trimethylsiloxy-ethoxy-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
 dimethylsilandiyl(2-trimethylsiloxy-ethoxy-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 dimethylsilandiyl(3-trimethylsiloxy-ethoxy-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 dimethylsilandiyl(2-trimethylsiloxy-ethoxy-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
 dimethylsilandiyl(3-trimethylsiloxy-ethoxy-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 20 dimethylsilandiylbis(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium dichloride;  
 dimethylsilandiylbis(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium dichloride;  
 dimethylsilandiyl(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium dichloride;
- 25 dimethylsilandiyl(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
 dimethylsilandiyl(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
 dimethylsilandiyl(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;
- 30 dimethylsilandiyl(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
 dimethylsilandiyl(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;

- dimethylsilandiyl(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-fluorenyl))  
zirconium dichloride;
- dimethylsilandiyl(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-fluorenyl))  
zirconium dichloride;
- 5 dimethylsilandiyl(3-(trimethylsiloxy-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
dimethylsilandiyl(3-(trimethylsiloxy-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methylbenzoindenyl))  
zirconium dichloride;
- dimethylsilandiylbis(1-(3-trimethylsiloxy-(dimethyl)silyl)-indenyl) zirconium dichloride;  
dimethylsilandiyl(1-(3-trimethylsiloxy-(dimethyl)silyl)-indenyl) (1-indenyl)zirconium dichloride;
- 10 isopropylidenebis(2-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;  
isopropylidenebis(3-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;  
isopropylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
isopropylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;
- 15 isopropylidene(1-(3-trimethylsiloxyethyl-indenyl)(cyclopentadienyl) zirconium dichloride;  
isopropylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
isopropylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
isopropylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
isopropylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
- 20 isopropylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
isopropylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
isopropylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium dichloride;
- isopropylidenebis(2-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;
- 25 isopropylidenebis(3-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;  
isopropylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
isopropylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
isopropylidene(1-(3-trimethylsiloxypropyl-indenyl)(cyclopentadienyl) zirconium dichloride;  
isopropylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;
- 30 isopropylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
isopropylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
isopropylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
isopropylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
isopropylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 35 isopropylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium dichloride;

- isopropylidenebis(2-(trimethylsiloxy-methoxy)-cyclopentadienyl) zirconium dichloride;  
isopropylidenebis(3-(trimethylsiloxy-methoxy)-cyclopentadienyl) zirconium dichloride;  
isopropylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
isopropylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
5 isopropylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
isopropylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
isopropylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
isopropylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
isopropylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
10 dichloride;  
isopropylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
dichloride;  
  
isopropylidenebis(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl) zirconium dichloride;  
15 isopropylidenebis(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl) zirconium dichloride;  
isopropylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
isopropylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
isopropylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
isopropylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
20 isopropylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
isopropylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
isopropylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
isopropylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
  
25 isopropylidenebis(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium dichloride;  
isopropylidenebis(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium dichloride;  
isopropylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
isopropylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
isopropylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
30 dichloride;  
isopropylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
dichloride;  
isopropylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl) zirconium  
dichloride;  
35

- isopropylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
- isopropylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 5 isopropylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- isopropylidene(3-(trimethylsiloxy-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium dichloride;
- isopropylidene(3-(trimethylsiloxy-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium dichloride;
- 10 ethylidenebis(2-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;
- ethylidenebis(3-trimethylsiloxyethyl-cyclopentadienyl) zirconium dichloride;
- ethylidene(3-trimethylsiloxyethyl-cyclopentadienyl) (cyclopentadienyl) zirconium dichloride;
- ethylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;
- 15 ethylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;
- ethylidene(1-(3-trimethylsiloxyethyl-indenyl))(cyclopentadienyl) zirconium dichloride;
- ethylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;
- ethylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;
- ethylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
- 20 ethylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
- ethylidene(2-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- ethylidene(3-trimethylsiloxyethyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- ethylidenebis(2-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;
- 25 ethylidenebis(3-trimethylsiloxypropyl-cyclopentadienyl) zirconium dichloride;
- ethylidene(3-trimethylsiloxypropyl-cyclopentadienyl) (cyclopentadienyl) zirconium dichloride;
- ethylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;
- ethylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(1-indenyl) zirconium dichloride;
- ethylidene(1-(3-trimethylsiloxypropyl-indenyl))(cyclopentadienyl) zirconium dichloride;
- 30 ethylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;
- ethylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;
- ethylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
- ethylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
- ethylidene(2-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 35 ethylidene(3-trimethylsiloxypropyl-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

ethylidenebis(2-(trimethylsiloxy-methoxy)-cyclopentadienyl) zirconium dichloride;  
ethylidenebis(3-(trimethylsiloxy-methoxy)-cyclopentadienyl) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
5 ethylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
10 ethylidene(3-(trimethylsiloxy-methoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

ethylidenebis(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl) zirconium dichloride;  
ethylidenebis(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
15 ethylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
20 ethylidene(2-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-ethoxy)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

ethylidenebis(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium dichloride;  
ethylidenebis(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl) zirconium dichloride;  
25 ethylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-indenyl) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
dichloride;  
ethylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
30 dichloride;  
ethylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
ethylidene(2-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
dichloride;

ethylidene(3-(trimethylsiloxy-ethyl-(dimethyl)silyl)-cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;

dimethylsilandiylbis(1-(2-trimethylsiloxyethyl-indenyl)) zirconium dichloride;

5 dimethylsilandiylbis(1-(3-trimethylsiloxyethyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

10 dimethylsilandiyl(1-(2-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

15 dimethylsilandiylbis(1-(2-trimethylsiloxypropyl-indenyl)) zirconium dichloride;

dimethylsilandiylbis(1-(3-trimethylsiloxypropyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

20 dimethylsilandiyl(1-(3-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

25

dimethylsilandiylbis(1-(2-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;

dimethylsilandiylbis(1-(3-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;

30 dimethylsilandiyl(1-(2-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(1-(3-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;

dimethylsilandiyl(1-(2-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

35 dimethylsilandiyl(1-(3-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

- dimethylsilandiylbis(1-(2-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;  
 dimethylsilandiylbis(1-(3-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;  
 dimethylsilandiyl(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;  
 dimethylsilandiyl(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;  
 5 dimethylsilandiyl(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 dimethylsilandiyl(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 dimethylsilandiyl(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
 dimethylsilandiyl(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
 dimethylsilandiyl(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;  
 10 dimethylsilandiyl(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- dimethylsilandiylbis(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;  
 dimethylsilandiylbis(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;  
 dimethylsilandiyl(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium dichloride;  
 15 dimethylsilandiyl(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium dichloride;  
 dimethylsilandiyl(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 dimethylsilandiyl(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 20 dimethylsilandiyl(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium dichloride;  
 dimethylsilandiyl(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium dichloride;  
 dimethylsilandiyl(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;  
 dimethylsilandiyl(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 25 dichloride;
- isopropylidenebis(1-(2-trimethylsiloxyethyl-indenyl)) zirconium dichloride;  
 isopropylidenebis(1-(3-trimethylsiloxyethyl-indenyl)) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;  
 30 isopropylidene(1-(3-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 isopropylidene(1-(3-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;  
 isopropylidene(1-(3-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;  
 35 isopropylidene(1-(2-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidenebis(1-(2-trimethylsiloxypropyl-indenyl)) zirconium dichloride;

isopropylidenebis(1-(3-trimethylsiloxypropyl-indenyl)) zirconium dichloride;

5 isopropylidene(1-(2-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;

10 isopropylidene(1-(3-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidenebis(1-(2-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;

15 isopropylidenebis(1-(3-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

20 isopropylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

25 isopropylidenebis(1-(2-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;

isopropylidenebis(1-(3-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

30 isopropylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;



- isopropylidenebis(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;  
 isopropylidenebis(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium dichloride;  
 isopropylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium dichloride;  
 5 isopropylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 isopropylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium dichloride;  
 10 isopropylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium dichloride;  
 isopropylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;  
 isopropylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;  
 15  
 ethylidenebis(1-(2-trimethylsiloxyethyl-indenyl)) zirconium dichloride;  
 ethylidenebis(1-(3-trimethylsiloxyethyl-indenyl)) zirconium dichloride;  
 ethylidene(1-(2-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;  
 ethylidene(1-(3-trimethylsiloxyethyl-indenyl))(1-indenyl) zirconium dichloride;  
 20 ethylidene(1-(2-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 ethylidene(1-(3-trimethylsiloxyethyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 ethylidene(1-(2-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;  
 ethylidene(1-(3-trimethylsiloxyethyl-indenyl))(9-fluorenyl) zirconium dichloride;  
 ethylidene(1-(2-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;  
 25 ethylidene(1-(3-trimethylsiloxyethyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;  
  
 ethylidenebis(1-(2-trimethylsiloxypropyl-indenyl)) zirconium dichloride;  
 ethylidenebis(1-(3-trimethylsiloxypropyl-indenyl)) zirconium dichloride;  
 ethylidene(1-(2-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;  
 30 ethylidene(1-(3-trimethylsiloxypropyl-indenyl))(1-indenyl) zirconium dichloride;  
 ethylidene(1-(2-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 ethylidene(1-(3-trimethylsiloxypropyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 ethylidene(1-(2-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;  
 ethylidene(1-(3-trimethylsiloxypropyl-indenyl))(9-fluorenyl) zirconium dichloride;  
 35 dichloride;

ethylidene(1-(2-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxypropyl-indenyl))(9-(2-methyl-fluorenyl) zirconium dichloride;  
dichloride.

- 5 ethylidenebis(1-(2-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride;  
ethylidenebis(1-(3-trimethylsiloxy-methoxy-indenyl)) zirconium dichloride,  
ethylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(1-indenyl) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
10 ethylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-methoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

- 15 ethylidenebis(1-(2-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;  
ethylidenebis(1-(3-trimethylsiloxy-ethoxy-indenyl)) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-indenyl) zirconium dichloride;  
20 ethylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-fluorenyl) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;  
25 ethylidene(1-(3-trimethylsiloxy-ethoxy-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

- ethylidenebis(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;  
ethylidenebis(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl)) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium dichloride;  
30 ethylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-indenyl) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
ethylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium dichloride;  
ethylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-fluorenyl) zirconium dichloride;

- ethylidene(1-(2-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- ethylidene(1-(3-trimethylsiloxy-ethyl-(dimethyl)silyl-indenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 5 dimethylsilylenebis(9-(1-trimethylsiloxyethyl-fluorenyl)) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxyethyl-fluorenyl))(cyclopentadienyl) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-indenyl) zirconium dichloride;
- 10 dimethylsilylene(9-(1-trimethylsiloxyethyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- dimethylsilylenebis(9-(1-trimethylsiloxypropyl-fluorenyl)) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-fluorenyl) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;
- 15 dimethylsilylene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-indenyl) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- dimethylsilylenebis(9-(1-trimethylsiloxy-methoxy-fluorenyl)) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;
- 20 dimethylsilylene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-indenyl) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- dimethylsilylenebis(9-(1-trimethylsiloxy-ethoxy-fluorenyl)) zirconium dichloride;
- 25 dimethylsilylene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-indenyl) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 30 dimethylsilylenebis(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl)) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-fluorenyl) zirconium dichloride;
- dimethylsilylene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;
- 35 dimethylsilylene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-indenyl) zirconium dichloride;

dimethylsilylene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidenebis(9-(1-trimethylsiloxyethyl-fluorenyl)) zirconium dichloride;

5 isopropylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-indenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

10 isopropylidenebis(9-(1-trimethylsiloxypropyl-fluorenyl)) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-indenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

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isopropylidenebis(9-(1-trimethylsiloxy-methoxy-fluorenyl)) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-indenyl) zirconium dichloride;

20

isopropylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidenebis(9-(1-trimethylsiloxy-ethoxy-fluorenyl)) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

25

isopropylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-indenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

isopropylidenebis(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl)) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-fluorenyl) zirconium dichloride;

30

isopropylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-indenyl) zirconium dichloride;

isopropylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;

35

- ethylidenebis(9-(1-trimethylsiloxyethyl-fluorenyl)) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(9-fluorenyl) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(1-indenyl) zirconium dichloride;  
 5 ethylidene(9-(1-trimethylsiloxyethyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- ethylidenebis(9-(1-trimethylsiloxypropyl-fluorenyl)) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-fluorenyl) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 10 ethylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(1-indenyl) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxypropyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- ethylidenebis(9-(1-trimethylsiloxy-methoxy-fluorenyl)) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;  
 15 ethylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(1-indenyl) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxy-methoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- ethylidenebis(9-(1-trimethylsiloxy-ethoxy-fluorenyl)) zirconium dichloride;  
 20 ethylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-fluorenyl) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-(2-methyl-indenyl)) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(1-indenyl) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxy-ethoxy-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 25 ethylidenebis(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl)) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-fluorenyl) zirconium dichloride;  
 ethylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-(2-methyl-indenyl)) zirconium  
 dichloride;  
 ethylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(1-indenyl) zirconium dichloride;  
 30 ethylidene(9-(1-trimethylsiloxy-ethyl-(dimethyl)silyl-fluorenyl))(9-(2-methyl-fluorenyl)) zirconium  
 dichloride;
- 35 trimethylsiloxyethyl(methyl)silandiylbis(cyclopentadienyl) zirconium dichloride;  
 trimethylsiloxyethyl(methyl)silandiylbis(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxyethyl(methyl)silandiyl(cyclopentadienyl)(1-indenyl) zirconium dichloride;

- trimethylsiloxyethyl(methyl)silandiyl(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
trimethylsiloxyethyl(methyl)silandiyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
trimethylsiloxyethyl(methyl)silandiyl(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
trimethylsiloxyethyl(methyl)silandiylbis(1-indenyl) zirconium dichloride;  
5 trimethylsiloxyethyl(methyl)silandiyl(cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium dichloride;  
trimethylsiloxyethyl(methyl)silandiylbis(1-(2-methylbenzoindenyl)) zirconium dichloride;
- trimethylsiloxypropyl(methyl)silandiylbis(cyclopentadienyl) zirconium dichloride;  
trimethylsiloxypropyl(methyl)silandiylbis(9-fluorenyl) zirconium dichloride;  
10 trimethylsiloxypropyl(methyl)silandiyl(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
trimethylsiloxypropyl(methyl)silandiyl(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
trimethylsiloxypropyl(methyl)silandiyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
trimethylsiloxypropyl(methyl)silandiyl(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
trimethylsiloxypropyl(methyl)silandiylbis(1-indenyl) zirconium dichloride;  
15 trimethylsiloxypropyl(methyl)silandiyl(cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium dichloride;
- trimethylsiloxy-methoxy(methyl)silandiylbis(cyclopentadienyl) zirconium dichloride;  
trimethylsiloxy-methoxy(methyl)silandiyl(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
trimethylsiloxy-methoxy(methyl)silandiyl(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
20 trimethylsiloxy-methoxy(methyl)silandiyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
trimethylsiloxy-methoxy(methyl)silandiyl(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- trimethylsiloxy-ethoxy(methyl)silandiylbis(cyclopentadienyl) zirconium dichloride;  
trimethylsiloxy-ethoxy(methyl)silandiyl(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
25 trimethylsiloxy-ethoxy(methyl)silandiyl(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
trimethylsiloxy-ethoxy(methyl)silandiyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
trimethylsiloxy-ethoxy(methyl)silandiyl(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiylbis(cyclopentadienyl) zirconium dichloride;  
30 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
dichloride;  
trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
35 dichloride;

- trimethylsiloxyethyl-(methyl)methylidenebis(cyclopentadienyl) zirconium dichloride;  
trimethylsiloxyethyl-(methyl)methylidene(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
trimethylsiloxyethyl-(methyl)methylidene(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
trimethylsiloxyethyl-(methyl)methylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
5 trimethylsiloxyethyl-(methyl)methylidene(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
trimethylsiloxyethyl-(methyl)methylidenebis(1-indenyl) zirconium dichloride;  
trimethylsiloxyethyl-(methyl)methylidene(cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium  
dichloride;
- 10 trimethylsiloxypropyl-(methyl)methylidenebis(cyclopentadienyl) zirconium dichloride;  
trimethylsiloxypropyl-(methyl)methylidene(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
trimethylsiloxypropyl-(methyl)methylidene(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
trimethylsiloxypropyl-(methyl)methylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
trimethylsiloxypropyl-(methyl)methylidene(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;  
15 trimethylsiloxypropyl-(methyl)methylidenebis(1-indenyl) zirconium dichloride;  
trimethylsiloxypropyl-(methyl)methylidene(cyclopentadienyl)(1-(2-methylbenzoindenyl)) zirconium  
dichloride;
- 20 trimethylsiloxy-methoxy(methyl)methylidenebis(cyclopentadienyl) zirconium dichloride;  
trimethylsiloxy-methoxy(methyl)methylidene(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
trimethylsiloxy-methoxy(methyl)methylidene(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium  
dichloride;  
trimethylsiloxy-methoxy(methyl)methylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
trimethylsiloxy-methoxy(methyl)methylidene(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
25 dichloride;
- 30 trimethylsiloxy-ethoxy-(methyl)methylidenebis(cyclopentadienyl) zirconium dichloride;  
trimethylsiloxy-ethoxy-(methyl)methylidene(cyclopentadienyl)(1-indenyl) zirconium dichloride;  
trimethylsiloxy-ethoxy-(methyl)methylidene(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;  
trimethylsiloxy-ethoxy-(methyl)methylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;  
trimethylsiloxy-ethoxy-(methyl)methylidene(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium  
dichloride;
- 35 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidenebis(cyclopentadienyl) zirconium dichloride;

- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidene(cyclopentadienyl)(1-indenyl) zirconium dichloride;
- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidene(cyclopentadienyl)(1-(2-methyl-indenyl)) zirconium dichloride;
- 5 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride;
- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidene(cyclopentadienyl)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylidenebis(1-indenyl) zirconium dichloride;
- 10 1-trimethylsiloxyethyl-ethylidenebis(cyclopentadienyl) zirconium dichloride;
- 1-trimethylsiloxyethyl-ethylidene-1-(cyclopentadienyl)-2-(1-indenyl) zirconium dichloride;
- 1-trimethylsiloxyethyl-ethylidene-1-(cyclopentadienyl)-2-(1-(2-methyl-indenyl)) zirconium dichloride;
- 1-trimethylsiloxyethyl-ethylidene-1-(cyclopentadienyl)-2-(9-fluorenyl) zirconium dichloride;
- 15 1-trimethylsiloxyethyl-ethylidene-1-(cyclopentadienyl)-2-(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 1-trimethylsiloxyethyl-ethylidenebis(1-indenyl) zirconium dichloride;
- 1-trimethylsiloxypropyl-ethylidenebis(cyclopentadienyl) zirconium dichloride;
- 1-trimethylsiloxypropyl-ethylidene-1-(cyclopentadienyl)-2-(1-indenyl) zirconium dichloride;
- 20 1-trimethylsiloxypropyl-ethylidene-1-(cyclopentadienyl)-2-(1-(2-methyl-indenyl)) zirconium dichloride;
- 1-trimethylsiloxypropyl-ethylidene-1-(cyclopentadienyl)-2-(9-fluorenyl) zirconium dichloride;
- 1-trimethylsiloxypropyl-ethylidene-1-(cyclopentadienyl)-2-(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 1-trimethylsiloxypropyl-ethylidenebis(1-indenyl) zirconium dichloride;
- 1-trimethylsiloxy-methoxy-ethylidenebis(cyclopentadienyl) zirconium dichloride;
- 25 1-trimethylsiloxy-methoxy-ethylidene-1-(cyclopentadienyl)-2-(1-indenyl) zirconium dichloride;
- 1-trimethylsiloxy-methoxy-ethylidene-1-(cyclopentadienyl)-2-(1-(2-methyl-indenyl)) zirconium dichloride;
- 1-trimethylsiloxy-methoxy-ethylidene-1-(cyclopentadienyl)-2-(9-fluorenyl) zirconium dichloride;
- 1-trimethylsiloxy-methoxy-ethylidene-1-(cyclopentadienyl)-2-(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 30 1-trimethylsiloxy-ethoxy-ethylidenebis(cyclopentadienyl) zirconium dichloride;
- 1-trimethylsiloxy-ethoxy-ethylidene-1-(cyclopentadienyl)-2-(1-indenyl) zirconium dichloride;
- 1-trimethylsiloxy-ethoxy-ethylidene-1-(cyclopentadienyl)-2-(1-(2-methyl-indenyl)) zirconium dichloride;
- 1-trimethylsiloxy-ethoxy-ethylidene-1-(cyclopentadienyl)-2-(9-fluorenyl) zirconium dichloride;
- 35 1-trimethylsiloxy-ethoxy-ethylidene-1-(cyclopentadienyl)-2-(9-(2-methyl-fluorenyl)) zirconium dichloride;



1-trimethylsiloxy-ethyl-(dimethyl)silyl ethylidenebis(cyclopentadienyl) zirconium dichloride;  
 1-trimethylsiloxy-ethyl-(dimethyl)silyl ethylidene-1-(cyclopentadienyl)-2-(1-indenyl) zirconium dichloride;  
 1-trimethylsiloxy-ethyl-(dimethyl)silyl ethylidene-1-(cyclopentadienyl)-2-(1-(2-methyl-indenyl)) zirconium dichloride

- 5 1-trimethylsiloxy-ethyl-(dimethyl)silyl ethylidene-1-(cyclopentadienyl)-2-(9-fluorenyl) zirconium dichloride,  
 1-trimethylsiloxy-ethyl-(dimethyl)silyl ethylidene-1-(cyclopentadienyl)-2-(9-(2-methyl-fluorenyl)) zirconium dichloride;

- 10 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(cyclopentadienyl) titanium dichloride;  
 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) titanium dichloride;  
 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-indenyl) titanium dichloride;  
 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;  
 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) titanium dichloride.

- 15 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;  
 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-(2-methylbenzoindenyl)) titanium dichloride;

(dimethyl)silandiyl-(tertbutylamido)(3-(trimethylsiloxyethylcyclopentadienyl) titanium dichloride;

- 20 (dimethyl)silandiyl-(tertbutylamido)(1-(3-trimethylsiloxyethylindenyl) titanium dichloride;

(dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(cyclopentadienyl) titanium dichloride;  
 (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(tetramethylcyclopentadienyl) titanium dichloride;  
 25 (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(1-indenyl) titanium dichloride;  
 (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(9-fluorenyl) titanium dichloride;  
 (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(1-(2-methylbenzoindenyl) titanium dichloride;

- trimethylsiloxypropyl(methyl)silandiyl(tertbutylamido)-(cyclopentadienyl) titanium dichloride;  
 30 trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) titanium dichloride;  
 trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(1-indenyl) titanium dichloride;  
 trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;  
 trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) titanium dichloride;  
 trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;  
 35 trimethylsiloxypropyl(methyl)silandiyl(tertbutylamido)-(1-(2-methylbenzoindenyl) titanium dichloride;

(dimethyl)silandiyl-(tertbutylamido)(3-(trimethylsiloxypropylcyclopentadienyl) titanium  
dichloride;

(dimethyl)silandiyl-(tertbutylamido)(1-(3-trimethylsiloxypropylindenyl) titanium  
dichloride;

5

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(cyclopentadienyl) titanium dichloride;

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(tetramethylcyclopentadienyl) titanium dichloride;

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(1-indenyl) titanium dichloride;

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(9-fluorenyl) titanium dichloride;

10

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(1-(2-methylbenzoindenyl) titanium dichloride;

trimethylsiloxy-methoxy (methyl)silandiyl-(tertbutylamido)(cyclopentadienyl) titanium dichloride;

trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) titanium  
dichloride,

15

trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;

trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) titanium dichloride;

trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;

20

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(cyclopentadienyl) titanium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) titanium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) titanium dichloride;

25

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(tertbutylamido)-(cyclopentadienyl) titanium  
dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl)  
titanium dichloride;

30

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) titanium  
dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) titanium dichloride;

35

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium  
dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(cyclopentadienyl) titanium dichloride;

5 trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) titanium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) titanium dichloride;

trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;

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trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(cyclopentadienyl) titanium dichloride;

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) titanium dichloride;

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(indenyl) titanium dichloride;

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(2-methyl-indenyl) titanium dichloride;

15

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) titanium dichloride;

trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(2-methyl-fluorenyl) titanium dichloride;

trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(cyclopentadienyl) titanium dichloride;

trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) titanium  
dichloride;

20

trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(1-indenyl) titanium dichloride;

trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;

trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(9-fluorenyl) titanium dichloride;

trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;

25

trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(cyclopentadienyl) titanium dichloride;

trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) titanium  
dichloride;

trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(1-indenyl) titanium dichloride;

30

trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;

trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(9-fluorenyl) titanium dichloride;

trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(cyclopentadienyl) titanium  
dichloride;

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- trimethylsiloxy-ethyl-(dimethyl)silyl (methyl) methylene (tertbutylamido) (tetramethylcyclopentadienyl) titanium dichloride;
- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(1-indenyl) titanium dichloride;
- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) titanium dichloride;
- 5 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) titanium dichloride;
- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) titanium dichloride;
- 10 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(cyclopentadienyl) zirconium dichloride;
- trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) zirconium dichloride;
- trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-indenyl) zirconium dichloride;
- trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride;
- trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) zirconium dichloride;
- 15 trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- trimethylsiloxyethyl(methyl)silandiyl-(tertbutylamido)(1-(2-methylbenzoindenyl)) zirconium dichloride;
- (dimethyl)silandiyl-(tertbutylamido)(3-(trimethylsiloxyethylcyclopentadienyl) zirconium dichloride;
- 20 (dimethyl)silandiyl-(tertbutylamido)(1-(3-trimethylsiloxyethylindenyl) zirconium dichloride;
- (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(cyclopentadienyl) zirconium dichloride;
- (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(tetramethylcyclopentadienyl) zirconium dichloride;
- 25 (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(1-indenyl) zirconium dichloride;
- (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(9-fluorenyl) zirconium dichloride;
- (dimethyl)silandiyl-(2-trimethylsiloxyethylamido)(1-(2-methylbenzoindenyl) zirconium dichloride;
- trimethylsiloxypropyl(methyl)silandiyl(tertbutylamido)-(cyclopentadienyl) zirconium dichloride;
- 30 trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) zirconium dichloride;
- trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(1-indenyl) zirconium dichloride;
- trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride;
- trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) zirconium dichloride;
- trimethylsiloxypropyl(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- 35 trimethylsiloxypropyl(methyl)silandiyl(tertbutylamido)-(1-(2-methylbenzoindenyl) zirconium dichloride;

(dimethyl)silandiyl-(tertbutylamido)(3-(trimethylsiloxypropyl)cylopentadienyl) zirconium dichloride;  
 (dimethyl)silandiyl-(tertbutylamido)(1-(3-trimethylsiloxypropyl)indenyl) zirconium dichloride;

(dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(cylopentadienyl) zirconium dichloride;  
 5 (dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(tetramethylcyclopentadienyl) zirconium dichloride,  
 (dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(1-indenyl) zirconium dichloride,  
 (dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(9-fluorenyl) zirconium dichloride;  
 (dimethyl)silandiyl-(3-trimethylsiloxypropylamido)(1-(2-methylbenzoindenyl) zirconium dichloride;

10 trimethylsiloxy-methoxy (methyl)silandiyl-(tertbutylamido)(cylopentadienyl) zirconium dichloride;  
 trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) zirconium  
 dichloride;

trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(1-indenyl) zirconium dichloride;  
 trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride;

15 trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxy-methoxy(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(cylopentadienyl) zirconium dichloride;  
 trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl) zirconium  
 20 dichloride;

trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(1-indenyl) zirconium dichloride;  
 trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride,  
 trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxy-ethoxy(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;

25 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl(tertbutylamido)-(cylopentadienyl) zirconium  
 dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-(tertbutylamido)(tetramethylcyclopentadienyl)  
 zirconium dichloride;

30 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(1-indenyl) zirconium dichloride.  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(1-(2-methyl-indenyl)) zirconium  
 dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)silandiyl-(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium  
 35 dichloride;

- trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(cyclopentadienyl) zirconium dichloride;  
 trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) zirconium dichloride;  
 trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(1-indenyl) zirconium dichloride;  
 trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride;  
 5 trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxyethyl-(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(cyclopentadienyl) zirconium dichloride;  
 trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) zirconium  
 10 dichloride;  
 trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(indenyl) zirconium dichloride;  
 trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(2-methyl-indenyl) zirconium dichloride;  
 trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxypropyl-(methyl)methylene(tertbutylamido)(2-methyl-fluorenyl) zirconium dichloride,  
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- trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(cyclopentadienyl) zirconium dichloride;  
 trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) zirconium  
 dichloride;  
 trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(1-indenyl) zirconium dichloride;  
 20 trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride;  
 trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(9-fluorenyl) zirconium dichloride;  
 trimethylsiloxy-methoxy(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(cyclopentadienyl) zirconium dichloride;  
 25 trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(tetramethylcyclopentadienyl) zirconium  
 dichloride;  
 trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(1-indenyl) zirconium dichloride;  
 trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) zirconium dichloride;  
 trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(9-fluorenyl) zirconium dichloride;  
 30 trimethylsiloxy-ethoxy-(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium dichloride;
- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(cyclopentadienyl) zirconium  
 dichloride;  
 trimethylsiloxy-ethyl-(dimethyl)silyl (methyl) methylene (tertbutylamido) (tetramethylcyclopentadienyl)  
 35 zirconium dichloride;

- trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(1-indenyl) zirconium dichloride;  
trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(1-(2-methyl-indenyl)) zirconium  
dichloride,  
trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(9-fluorenyl) zirconium dichloride;  
5 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl)methylene(tertbutylamido)(9-(2-methyl-fluorenyl)) zirconium  
dichloride,
- trimethylsiloxyethyl(methyl) silandiyl-oxo(cyclopentadienyl) titanium dichloride;  
trimethylsiloxyethyl(methyl) silandiyl-oxo-(tetramethylcyclopentadienyl) titanium dichloride;  
10 trimethylsiloxyethyl(methyl) silandiyl-oxo(1-indenyl) titanium dichloride;  
trimethylsiloxyethyl(methyl) silandiyl-oxo(1-(2-methyl-indenyl)) titanium dichloride;  
trimethylsiloxyethyl(methyl) silandiyl-oxo(9-fluorenyl) titanium dichloride;  
trimethylsiloxyethyl(methyl) silandiyl-oxo(9-(2-methyl-fluorenyl)) titanium dichloride;
- 15 trimethylsiloxypropyl(methyl) silandiyl-oxo(cyclopentadienyl) titanium dichloride;  
trimethylsiloxypropyl(methyl) silandiyl-oxo(tetramethylcyclopentadienyl) titanium dichloride;  
trimethylsiloxypropyl(methyl) silandiyl-oxo(1-indenyl) titanium dichloride;  
trimethylsiloxypropyl(methyl) silandiyl-oxo(1-(2-methyl-indenyl)) titanium dichloride;  
trimethylsiloxypropyl(methyl) silandiyl-oxo(9-fluorenyl) titanium dichloride;  
20 trimethylsiloxypropyl(methyl) silandiyl-oxo(9-(2-methyl-fluorenyl)) titanium dichloride;
- trimethylsiloxy-methoxy(methyl) silandiyl-oxo(cyclopentadienyl) titanium dichloride;  
trimethylsiloxy-methoxy(methyl) silandiyl-oxo(tetramethylcyclopentadienyl) titanium dichloride;  
trimethylsiloxy-methoxy(methyl) silandiyl-oxo(1-indenyl) titanium dichloride;  
25 trimethylsiloxy-methoxy(methyl) silandiyl-oxo(1-(2-methyl-indenyl)) titanium dichloride;  
trimethylsiloxy-methoxy(methyl) silandiyl-oxo(9-fluorenyl) titanium dichloride;  
trimethylsiloxy-methoxy(methyl) silandiyl-oxo(9-(2-methyl-fluorenyl)) titanium dichloride;
- trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(cyclopentadienyl) titanium dichloride;  
30 trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(tetramethylcyclopentadienyl) titanium dichloride;  
trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(1-indenyl) titanium dichloride;  
trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(1-(2-methyl-indenyl)) titanium dichloride;  
trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(9-fluorenyl) titanium dichloride;  
trimethylsiloxy-ethoxy(methyl) silandiyl-oxo(9-(2-methyl-fluorenyl)) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(cyclopentadienyl) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(tetramethylcyclopentadienyl) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(1-indenyl) titanium dichloride;

5 trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(1-(2-methyl-indenyl)) titanium dichloride;

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(fluorenyl) titanium dichloride,

trimethylsiloxy-ethyl-(dimethyl)silyl-(methyl) silandiyl-oxo(9-methylfluorenyl) titanium dichloride

10 The metallocene compounds according to the invention can be prepared according to the methods disclosed in EP 97500187.6 which is herewith enclosed by reference.

Supports useful in the preparation of the heterogeneous catalyst of the invention are inorganic oxides, such as: silica, alumina, silica alumina, aluminum phosphates and mixtures thereof, which result in supported catalysts with contents in transition metal between 0.01 and 10% by weight, preferably between 0.1 and 1%.

15 The inorganic oxide, before treatment with the metallocene, is treated in such a way that it has deposited on its surface an alumoxane. Alumoxanes suitable for the preparation of the support are those represented by the formulas:



20

wherein R is alkyl or aryl group containing from 1 to 20 carbon atoms; n ranges from 1 to 40, preferably from 5 to 20 and m ranges from 3 to 40 preferably from 3 to 20.

Generally, in the preparation of alumoxane from, for example, aluminum trimethyl and water, a mixture of linear and cyclic compounds are obtained.

25 The alumoxane can be prepared in a variety of ways. For example, they are prepared by contacting water with a solution of aluminum trialkyl, such as, for example aluminum trimethyl, in a suitable organic solvent such as benzene or an aliphatic hydrocarbon.

The treatment of the inorganic porous support can be done according to any method known in the art. For example the alumoxane can be deposited onto the surface of the inorganic support by dissolving the alumoxane into a suitable solvent and adding the inorganic support into the solution, or it can be deposited  
30 onto the surface of the porous support by precipitation in the presence of the support.

It is also possible to form the alumoxane directly on the surface of the porous support by reacting an aluminum alkyl with the hydration water present onto the support surface.

35 A method that can be fit for preparing supported catalysts according to this invention consists in the impregnation, under anhydrous conditions and inert atmosphere, of the solution of any metallocene of



formula I, II or III, or a mixture thereof, on the treated supporting material at a proper temperature, preferably between  $-20^{\circ}\text{C}$  and  $90^{\circ}\text{C}$ . The supported catalyst that contains the metallocene can be obtained through filtration and washing with a proper solvent, preferably an aliphatic or aromatic hydrocarbon without polar groups.

5 Another method that can properly be used consists in depositing the metallocene on the treated support by using a solution of the compound that has to be heterogenized, eliminating the solvent through evaporation and then warming the solid residue at a temperature between  $25$  and  $150^{\circ}\text{C}$ . Besides, the resulting residue, obtained by this process, can be subjected to washing and subsequent filtration.

10 The supported catalyst does not require addition of alumoxane or ionizing compound to the reactor, but only a certain amount of aluminium trialkyl. This fact constitutes a further clear advantage in view of most polymerization process which require large amounts of aluminoxane.

The most proper polymerization procedure can change according to the chosen type of polymerization process (suspension, gas phase, solution or in bulk).

15 For the polymerization in suspension, the cocatalyst can previously be mixed with the supported solid catalyst, can be added to the polymerization medium before the supported catalyst, or both operations can be sequentially realized.

The process consists in putting in contact the monomer, or, in certain cases, the monomer and the comonomer, with a catalytic composition according to the present invention, that includes at least one supported metallocene complex of formula I, II or III, at a proper temperature and pressure.

20 Suitable olefins that can be used as comonomers to obtain ethylene copolymers are  $\alpha$ -olefins such as propylene, butene, hexene, octene, 4-methyl-1-pentene and cyclic olefins and can be used in proportions from 0.1 to 70% by weight of the total of the monomers. In the case of homopolymerization of ethylene, the density of polymers ranges between  $0,950$  and  $0,965\text{ g/cm}^3$ ; in the case of copolymerization of ethylene, the density is as low as  $0,900\text{ g/cm}^3$ .

25 To control the molecular weight of the obtained polymers, hydrogen can optionally be used as a chain transfer agent in such proportions that the hydrogen partial pressure, with respect to the olefin one, be from 0.01 to 50%.

In the particular case of the polymerization technique known as suspension process or controlled particle morphology process, the used temperature will be between  $30^{\circ}$  and  $100^{\circ}\text{C}$ , the same which is typically used in gas phase.

30 The used pressure changes according to the polymerization technique; it ranges from atmospheric pressure to  $350\text{ MPa}$ .

35 It has been surprisingly found that the presence of the group  $-\text{OSiR}^{\text{II}}_3$  is essential in order to obtain excellent results in term of catalyst activity. If a group  $\text{Si-Cl}$  is present on the metallocene instead of the group  $\text{R}^{\text{I}}\text{OSiR}^{\text{II}}_3$ , the result is clearly inferior. Although it is not yet possible to describe exactly the

interaction taking place between alumoxane and trialkylsiloxo group, it seems very clear that it results in a catalyst presenting unique balance between activity of the catalyst and morphology of the obtained polymer, even better than the results disclosed in patent EP 97500187.6.

The activity of the catalyst according to the invention has been measured in homogeneous catalysis and onto silica impregnated with MAO. The same conditions have been used for metallocenes containing a Si-Cl group and for metallocenes which do not contain a functional group which can react with silica. Table I shows that the metallocene according to the invention is slightly less active under homogeneous condition than the corresponding non-functionalized metallocene, but it becomes much more active when supported onto treated silica. The same conclusions apply when comparing the metallocene according to the invention with the metallocene containing a Si-Cl group.

The following examples are described in order to better understand the invention. The materials, the chemical compounds and the conditions used in these examples are illustrative and do not limit the scope of the invention.

## EXAMPLES

### PREPARATION OF SUPPORTED FUNCTIONALIZED METALLOCENES

#### EXAMPLE 1

*Heterogenization of (3-trimethylsiloxypentadienyl) (cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of (3-trimethylsiloxypentadienyl) (cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,29 % and 19,4 % by weight respectively.

#### COMPARATIVE EXAMPLE 2

*Heterogenization of (chlorodimethylsilylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of

(chlorodimethylsilylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,40 % and 20,7 % by weight respectively.

### EXAMPLE 3

*Heterogenization of (chloromethylsilyl)bis(cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of (chloromethylsilyl)bis(cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,36 % and 18,1 % by weight respectively.

### PREPARATION OF SUPPORTED NON-FUNCTIONALIZED METALLOCENES

#### EXAMPLE 4

*Heterogenization of bis(cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of bis(cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,36 % and 18,4 % by weight respectively.

#### EXAMPLE 5

*Heterogenization of (trimethylsilyl)cyclopentadienyl (cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of (trimethylsilyl)cyclopentadienyl (cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction

mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,4 % and 21,2 % by weight respectively.

5

#### EXAMPLE 6

*Heterogenization of (dimethylsilandiyl)bis(cyclopentadienyl) zirconium dichloride on silica modified with MAO.*

In a flask of 250 ml of capacity it was weighed 5 g of silica modified with MAO commercialized by Witco with a 24,7% weight of Al and it was added 120 ml of toluene. Then, it was added a solution in toluene of (dimethylsilandiyl)bis(cyclopentadienyl) zirconium dichloride (0,255 mmol of Zr). The reaction mixture was maintained under mechanic stirring at room temperature. After 2 hours of reaction the resulting solid was isolated by filtration and washed with consecutive fractions of toluene at 70° C up to a total volume of 500 ml. The solid was finally dried under vacuum for 24 hours. The Zr and Al content in the catalyst was determined by ICP and it was 0,37 % and 20,8 % by weight respectively.

15

### POLYMERIZATION WITH FUNCTIONALIZED SOLUBLE CATALYSTS

#### EXAMPLE 7

*Copolymerization of ethylene/1-hexene*

The reactions of copolymerization of ethylene/1-hexene were carried out in a reactor Büchi of 1,3 liters of capacity, under anhydrous conditions. The reactor, charged with 600 ml of dry heptane, was conditioned at 70°C and pressurized with ethylene up to 4 atm. Then, it was added 20 ml of 1-hexene, 2,7 ml of a solution of MAO 10% in toluene (commercialized by Witco) and finally 0,42 ml of a solution  $4,7 \times 10^{-3}$  M in toluene of (3-trimethylsiloxy propyl cyclopentadienyl) (cyclopentadienyl) zirconium dichloride (0,002 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 10,4 g of polyethylene (activity  $5,2 \times 10^6$  g PE/mol M x h x atm) with a Mw of 172.800, MWD of 4 and a comonomer content of 1,77% molar.

25

30

#### EXAMPLE 8

*Polymerization of ethylene*

The polymerization reaction of ethylene was carried out in a reactor Büchi of 1,3 liters of capacity, under anhydrous conditions. The reactor, charged with 600 ml of dry heptane, was conditioned at 70°C and pressurized with ethylene up to 4 atm. Then, it was added 1,1 ml of a solution of MAO 10% in toluene

35

(commercialized by Witco) and 0,28 ml of a solution  $2,8 \times 10^{-3}$  M in toluene of (chlorodimethylsilylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride (0,0008 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 8,1 g of polyethylene (activity  $10,0 \times 10^6$  g PE/mol M x h x atm) with a Mw of 288.300 and MWD 2.2.

#### EXAMPLE 9

##### *Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 8, but it was added 5,3 ml of a solution of MAO 10% in toluene (commercialized by Witco) and 0,93 ml of a solution  $4,3 \times 10^{-3}$  M in toluene of (chloromethylsilyl) bis (cyclopentadienyl) zirconium dichloride (0,004 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 5,1 g of polyethylene (activity  $1,3 \times 10^6$  g PE/mol M x h x atm) with a Mw of 162.000.

#### POLYMERIZATION WITH NON-FUNCTIONALIZED SOLUBLE CATALYSTS

#### EXAMPLE 10

##### *Copolymerization of ethylene/1-hexene*

The reaction of copolymerization of ethylene with 1-hexene was carried out by following the method and the conditions described in example 7, but it was added 2,7 ml of a solution of MAO 10% in toluene commercialized by Witco and finally 0,7 ml of a solution in toluene ( $2,7 \times 10^{-3}$  M) of biscyclopentadienyl zirconium dichloride (0,002 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 16 g of polyethylene (activity  $8,0 \times 10^6$  g PE/mol M x h x atm) with a Mw of 59.300, MWD 2.4 and a comonomer content of 1,08% molar.

#### EXAMPLE 11

##### *Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 8, but it was added 1,1 ml of a solution of MAO 10% in toluene (commercialized by Witco) and then 0,3 ml of a solution in toluene ( $3,0 \times 10^{-3}$  M) of (trimethylsilylcyclopentadienyl) (cyclopentadienyl) zirconium dichloride (0,0008 mmol of Zr). The polymerization reaction was maintained

at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 13,5 g of polyethylene (activity  $16,9 \times 10^6$  g PE/mol M x h x atm) with a Mw of 319.200 and MWD 2.3.

5      EXAMPLE 12

*Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 8, but it was added 5,3 ml of a solution of MAO 10% in toluene commercialized by Witco and finally 0,87 ml of a solution in toluene ( $4,6 \times 10^{-3}$  M) of (dimethylsilandyil)bis(cyclopentadienyl) zirconium dichloride (0,004 mmol of Zr). The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 11,7 g of polyethylene (activity  $2,90 \times 10^6$  g PE/mol M x h x atm) with a Mw of 64.500 and MWD 3.5.

15      POLYMERIZATION WITH FUNCTIONALIZED SUPPORTED CATALYSTS

EXAMPLE 13

*Copolymerization of ethylene/1-hexene*

The reactions of copolymerization of ethylene with 1-hexene were carried out in a reactor Büchi of 1,3 liters of capacity, under anhydrous conditions. The reactor, charged with 600 ml of dry heptane, was conditioned at 70°C and pressurized with ethylene up to a pressure of 3,5 atm, then it was added 20 ml of 1-hexene, 1,7 ml of a solution of TIBA 1,34 M in heptane and it was finally added, through a overpressure of ethylene of 0,5 atm, 0,179 g (0,0057 mmol of Zr) of the catalyst prepared according to example 1. The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 13,8 g of polyethylene (activity  $2,4 \times 10^6$  g PE/mol M x h x atm) with a Mw of 178.600, a MWD of 2,4 and a comonomer content of 2,27% molar.

EXAMPLE 14

30      *Polymerization of ethylene*

The reactions of polymerization of ethylene were carried out in a reactor Büchi of 1,3 liters of capacity, under anhydrous conditions. The reactor, charged with 600 ml of dry heptane, was conditioned at 70°C and pressurized with ethylene up to a pressure of 3,5 atm. Later, it was added 1,7 ml of a solution of TIBA 1,34 M in heptane and it was finally added, through a overpressure of ethylene of 0,5 atm, 0,130 g (0,0057 mmol of Zr) of the catalyst described in example 2. The polymerization reaction was maintained at 70°C

and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 6 g of polyethylene (activity  $1,1 \times 10^6$  g PE/mol M x h x atm) with a Mw of 378.500 and MWD 2.6.

5 EXAMPLE 15

*Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 14, but it was added 2,4 ml of a solution of TIBA 1,34 M in heptane and 0,203 g (0,008 mmol of Zr) of the catalyst described in example 3. The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 2,5 g of polyethylene (activity  $0,32 \times 10^6$  g PE/mol M x h x atm) with a Mw of 159.600 and MWD 5.3.

15 POLYMERIZATION WITH NON-FUNCTIONALIZED SUPPORTED CATALYSTS

EXAMPLE 16

*Copolymerization of ethylene/ 1-hexene*

The reaction of copolymerization of ethylene with 1-hexene was carried out by following the method and the conditions described in example 13, but it was added 0,144 g (0,0057 mmol of Zr) of the catalyst described in example 4. The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 2,8 g of polyethylene (activity  $0,5 \times 10^6$  g PE/mol M x h x atm) with a Mw of 157.900, (MWD) of 3,7 and a comonomer content of 1,53% molar.

25 EXAMPLE 17

*Polymerization of ethylene*

The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 14, but it was added 0,130 g (0,0057 mmol of Zr) of the catalyst described in example 5. The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 6,2 g of polyethylene (activity  $1,1 \times 10^6$  g PE/mol M x h x atm) with a Mw of 327.600 and MWD 2.3.

EXAMPLE 18

35 *Polymerization of ethylene*


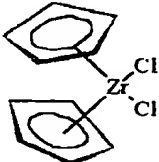
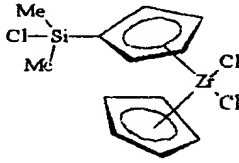
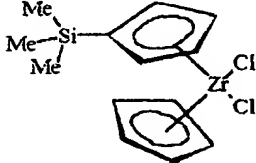
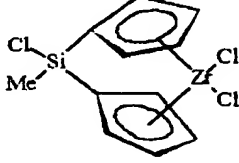
The polymerization reaction of ethylene was carried out by following the method and the conditions described in example 14, but it was added 2,4 ml of a solution of TIBA 1,34 M in heptane and 0,179 g (0,008 mmol of Zr) of the catalyst prepared according to example 6. The polymerization reaction was maintained at 70°C and a pressure of 4 atm for 15 minutes. At the end of the reaction, the reactor was depressurized and the obtained product was treated with acidified methanol. It was obtained 2,4 g of polyethylene (activity  $0,3 \times 10^6$  g PE/mol M x h x atm) with a Mw of 86.900 and MWD 4.7.

#### EXAMPLE 19

##### *Copolymerization of ethylene/1-hexene in Autoclave*

The reaction of copolymerization of ethylene with 1-hexene was carried out in an autoclave of a capacity of 2 liters, under anhydrous conditions. The reactor, charged with 1 l of dry isobutane, 124 ml of 1-hexene and 0,6 ml of a solution of TIBA 1,34 M in heptane, was conditioned at a temperature of 90°C. Later, it was added 0,1 g (0,003 mmol of Zr) of the catalyst prepared according to example 1 and the reactor was pressurized with ethylene up to a total pressure of 40 atm. The copolymerization reaction was maintained at 90°C and at a pressure of 40 atm for 60 minutes. At the end of the reaction, the reactor was depressurized and it was obtained 365 g of polyethylene (activity  $5 \times 10^6$  g PE/mol M x h x atm) with a Mw of 135.000, MWD of 2, a comonomer content of 1% molar, an bulk density of 0,3 g/cc, a particle medium size of 0,6 mm and a distribution of particles sizes as it is shown in fig. 1.



TYPE OF CATALYST	EXAMPLE	METALLOCENE	ACTIVITY $\times 10^6$
Homogeneous	7		5,2
Heterogeneous	13		2,4
Homogeneous	10		8,0
Heterogeneous	16		0,49
Homogeneous	8		10
Heterogeneous	14		1,1
Homogeneous	11		16,9
Heterogeneous	17		1,1
Homogeneous	9		1,3
Heterogeneous	15		0,32

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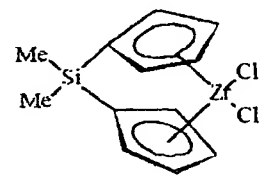
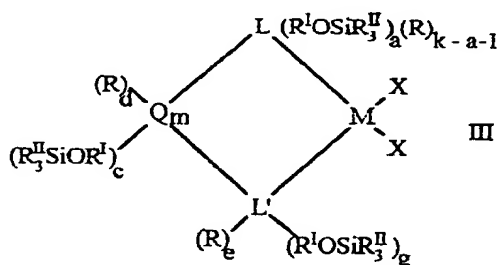
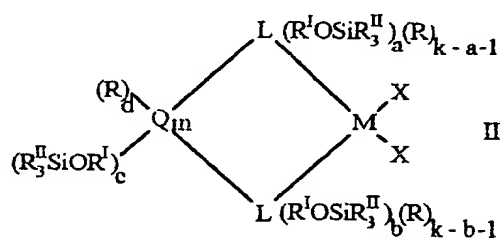
Homogeneous	12		2,9
Heterogeneous	18		0,3

Table I

## CLAIMS

1.- Heterogeneous catalytic system obtainable by reacting a porous inorganic support with an alumoxane and subsequently supporting at least one metallocene compound thereon, characterized in that the metallocene compound is defined by the following general formulas:



wherein:

L, equal to or different from each other, is selected from the group comprising: cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl or benzoindenyl;

each R is independently selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl, linear or branched, optionally substituted by 1 to 10 halogen atoms, or a group SiR<sup>II</sup><sub>3</sub>;

each R<sup>I</sup>, equal to or different from each other, is a divalent aliphatic or aromatic hydrocarbon group containing from 1 to 20 carbon atoms, optionally containing from 1 to 5 heteroatoms of groups 14 to 16 of the periodic table of the elements and boron; preferably it is: C<sub>1</sub>-C<sub>20</sub> alkylene, C<sub>3</sub>-C<sub>20</sub> cycloalkylene, C<sub>6</sub>-C<sub>20</sub> arylene, C<sub>7</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkylene, or alkylarylene, linear or branched, or a group SiR<sup>II</sup><sub>2</sub>;

each R<sup>II</sup> is independently selected from C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl or C<sub>7</sub>-C<sub>20</sub> alkylaryl, linear or branched; preferably R<sup>II</sup> is methyl, ethyl, isopropyl;

each Q is independently selected from B, C, Si, Ge, Sn;

M is a metal of group 3, 4 or 10 of the Periodic Table, Lanthanide or Actinide;

each X is independently selected from: hydrogen, chlorine, bromine,  $OR^II$ ,  $NR^II$ ,  $C_1-C_{20}$  alkyl or  $C_6-C_{20}$  aryl;

$L'$  is N or O;

when L is cyclopentadienyl k is equal to 5, when L is indenyl k is equal to 7, when L is fluorenyl or benzoindenyl k is equal to 9, when L is tetrahydroindenyl k is equal to 11 and when L is octahydrofluorenyl, k is equal to 17;

z is equal to 0, 1 or 2;

x is equal to 1, 2 or 3;

y is equal to 1, 2 or 3;

x + y + z is equal to the valence of M;

m is an integer which can assume the values 1, 2, 3 or 4;

a and b are integers whose value ranges from 0 to k-1;

f is an integer whose value ranges from 1 to k;

g is 0 or 1;

c and e are equal to 0 or 1;

a + b + c is at least 1;

a + g + c is at least 1;

d is equal to 0, 1 or 2;

when Q is B then c + d = 1;

when Q is C, Si, Ge or Sn, then c + d = 2;

when  $L'$  is N, then g + e = 1;

when  $L'$  is O, then g = 0 and e = 0.

2.- Heterogeneous catalytic system according to claim 1 wherein the group  $R^I OSiR^II_3$  is selected from  $CH_3-CH_2-OSiMe_3$ ,  $CH_3-CH_2-CH_2-OSiMe_3$ ,  $CH_2-O-CH_2-OSiMe_3$ ,  $O-CH_2-CH_2-OSiMe_3$ ,  $SiMe_2-CH_2-CH_2-OSiMe_3$ ,  $SiMe_2-OSiMe_3$ .

3.- Heterogeneous catalytic system according to claim 1 or 2 wherein  $R^II$  is methyl, ethyl, isopropyl;

4.- Heterogeneous catalytic system according to claims 1-3 wherein M is titanium, zirconium or hafnium;

5.- Heterogeneous catalytic system according to claims 1-4 wherein the alumoxane is represented by the formulas:



wherein R is alkyl or aryl group containing from 1 to 20 carbon atoms; n ranges from 1 to 40, and m ranges from 3 to 40.

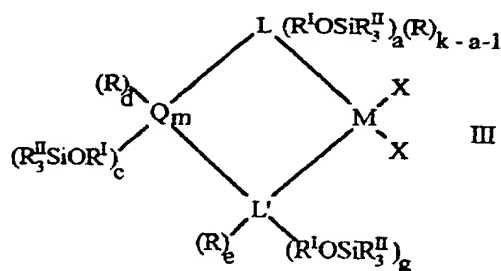
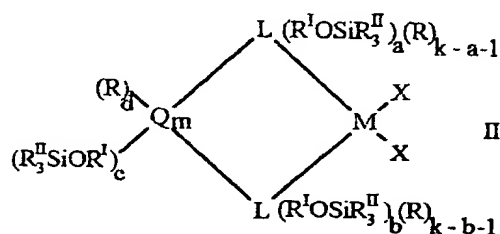
6.- Heterogeneous catalyst system according to claims 1-5 wherein the inorganic support is selected from silica, alumina, silica alumina, aluminium phosphates and mixtures thereof,

7.- Heterogeneous catalyst system according to claims 1-6 wherein the content in transition metal is comprised between 0.01 and 10% by weight.

5 8.- Heterogeneous catalyst system according to claim 7 wherein the content in transition metal is comprised between 0.1 and 1% by weight.

9.- Process for the polymerization of alpha olefins in slurry or in gas phase characterized by the use of the heterogeneous catalyst system of claims 1-8.

10.- Metallocene compounds according to the following formulas:



wherein:

L, equal to or different from each other, is selected from the group comprising: cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl and benzoindenyl;

each R is independently selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl, linear or branched, optionally substituted by 1 to 10 halogen atoms, or a group SiR''<sub>3</sub>;

each R<sup>I</sup>, equal to or different from each other, is a divalent aliphatic or aromatic hydrocarbon group containing from 1 to 20 carbon atoms, optionally containing from 1 to 5 heteroatoms of groups 14 to 16 of the periodic table of the elements and boron; preferably it is: C<sub>1</sub>-C<sub>20</sub> alkylene, C<sub>3</sub>-C<sub>20</sub> cycloalkylene, C<sub>6</sub>-C<sub>20</sub> arylene, C<sub>7</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkylene, or alkylarylene, linear or branched, or a group SiR''<sub>2</sub>;

each  $R''$  is independently selected from  $C_1-C_{20}$  alkyl,  $C_3-C_{20}$  cycloalkyl,  $C_6-C_{20}$  aryl,  $C_3-C_{20}$  alkenyl,  $C_7-C_{20}$  arylalkyl,  $C_8-C_{20}$  arylalkenyl or  $C_7-C_{20}$  alkylaryl, linear or branched; preferably  $R''$  is methyl, ethyl, isopropyl;

each Q is independently selected from B, C, Si, Ge, Sn;

5 M is a metal of group 3, 4 or 10 of the Periodic Table, Lanthanide or Actinide; preferably it is titanium, zirconium or hafnium;

each X is independently selected from: hydrogen, chlorine, bromine,  $OR''$ ,  $NR''_2$ ,  $C_1-C_{20}$  alkyl or  $C_6-C_{20}$  aryl;

$L'$  is N or O

10 when L is cyclopentadienyl k is equal to 5, when L is indenyl k is equal to 7, when L is fluorenyl or benzoindenyl k is equal to 9, when L is tetrahydroindenyl k is equal to 11 and when L is octahydrofluorenyl, k is equal to 17;

z is equal to 0, 1 or 2;

x is equal to 1, 2 or 3;

15 y is equal to 1, 2 or 3;

$x + y + z$  is equal to the valence of M;

m is an integer which can assume the values 1, 2, 3 or 4;

a and b are integers whose value ranges from 0 to k-1;

f is an integer whose value ranges from 1 to k;

20 g is equal to 0 or 1;

c and e are equal to 0 or 1;

$a + b + c$  is at least 1;

$a + g + c$  is at least 1;

d is equal to 0, 1 or 2;

25 when Q is B then  $c + d = 1$ ;

when Q is C, Si, Ge or Sn, then  $c + d = 2$ ;

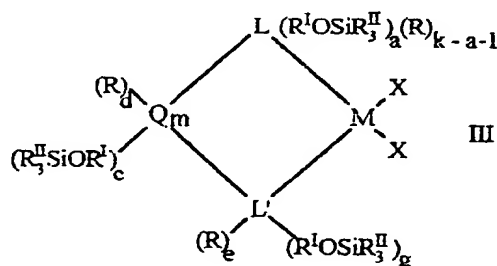
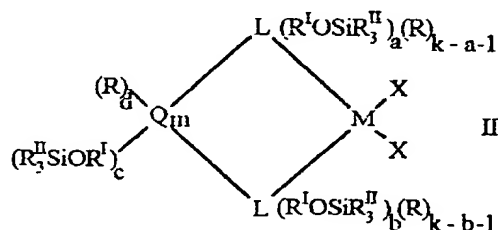
when  $L'$  is N, then  $g + e = 1$ ;

when  $L'$  is O, then  $g = 0$  and  $e = 0$ .

30 characterized in that at least one L is a fluorenyl, benzoindenyl or octahydrofluorenyl ring, optionally substituted by  $C_1-C_{20}$  alkyl,  $C_3-C_{20}$  cycloalkyl,  $C_6-C_{20}$  aryl,  $C_3-C_{20}$  alkenyl,  $C_7-C_{20}$  arylalkyl,  $C_8-C_{20}$  arylalkenyl or  $C_7-C_{20}$  alkylaryl.

## ABSTRACT

The invention relates to heterogeneous catalytic systems obtainable by reacting a porous inorganic support with an alumoxane and subsequently supporting at least one metallocene compound thereon, characterized in that the metallocene compound is defined by the following general formulas:



wherein:

L, equal to or different from each other, is selected from the group comprising: cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl or benzoindenyl; each R is independently selected from hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl, linear or branched, optionally substituted by 1 to 10 halogen atoms, or a group SiR<sup>II</sup><sub>3</sub>; each R<sup>I</sup>, equal to or different from each other, is a divalent aliphatic or aromatic hydrocarbon group containing from 1 to 20 carbon atoms, optionally containing from 1 to 5 heteroatoms of groups 14 to 16 of the periodic table of the elements and boron; preferably it is: C<sub>1</sub>-C<sub>20</sub> alkylene, C<sub>3</sub>-C<sub>20</sub> cycloalkylene, C<sub>6</sub>-C<sub>20</sub> arylene, C<sub>7</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkylene, or alkylarylene, linear or branched, or a group SiR<sup>II</sup><sub>2</sub>; each R<sup>II</sup> is independently selected from C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>3</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> aryl, C<sub>3</sub>-C<sub>20</sub> alkenyl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, C<sub>8</sub>-C<sub>20</sub> arylalkenyl or C<sub>7</sub>-C<sub>20</sub> alkylaryl, linear or branched; preferably R<sup>II</sup> is methyl, ethyl, isopropyl; each Q is independently selected from B, C, Si, Ge, Sn; M is a metal of group 3, 4 or 10 of the Periodic Table, Lanthanide or Actinide; preferably it is titanium, zirconium or hafnium; each X is independently selected from: hydrogen, chlorine, bromine, OR<sup>II</sup>, NR<sup>II</sup><sub>2</sub>, C<sub>1</sub>-C<sub>20</sub> alkyl or C<sub>6</sub>-C<sub>20</sub> aryl; L' is

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5 N or O; z is equal to 0, 1 or 2; x is equal to 1, 2 or 3; y is equal to 1, 2 or 3;  $x + y + z$  is equal to the valence of M; m is an integer which can assume the values 1, 2, 3 or 4; a and b are integers whose value ranges from 0 to k-1, f is an integer whose value ranges from 1 to k; g is an integer whose value ranges from 0 to 1; c and e are equal to 0 or 1;  $a + b + c$  is at least 1;  $a + g + c$  is at least 1; d is equal to 0, 1 or 2; when Q is B then  $c + d = 1$ ; when Q is C, Si, Ge or Sn, then  $c + d = 2$ ; when L' is N, then  $g + e = 1$ ; when L' is O, then  $g = 0$  and  $e = 0$ .

The invention also relates to the polymerization process making use of the above defined catalytic system.

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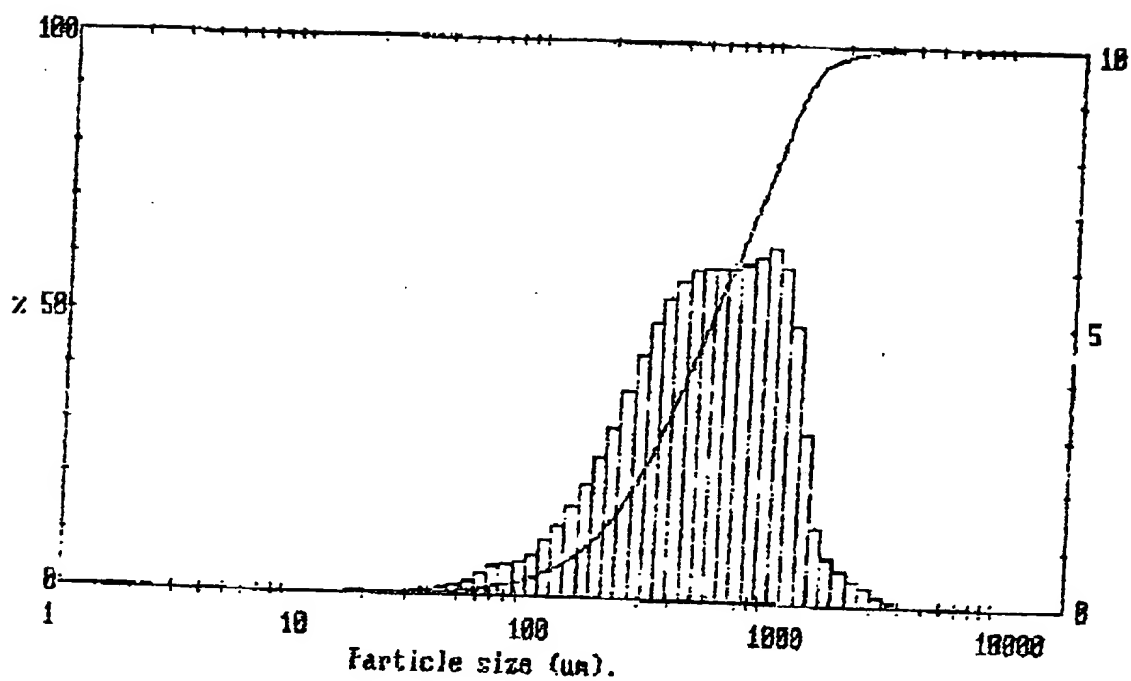
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Fig. 1



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